Influence of the electroplating pretreatment on corrosion mechanism of NdFeB magnets

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Abstract: The electroplating pretreatment of NdFeB magnets was simulated in this study, and the effect of the pickling process on element, matrix morphology and texture was discussed. The results showed that in the ordinary circumstance the acid solution concentration should be below 4 mol/L and the pickling time was within 120 s. However the concentration was lower than 1 mol/L and the time was about 30 s in the ultrasonic environment. The precoating technology sequentially was studied. The results revealed that there were two main reactions of the corrosion and displacement in the precoating process, and these two reactions were more obvious in the grain boundary. The electrochemical analysis illustrated that the corrosion and displacement reactions were affected obviously by the current density and the precoating solution temperature, usually the current density was controlled about 0.3 A/dm^2, and the temperature was about 318 K in the precoating process.

Keywords: NdFeB magnet; pickling; precoating; corrosion; pretreatment; rare earths

NdFeB magnets have attracted increasing attention in recent years due to their excellent magnetic properties. However, their poor corrosion resistance in climatic and corrosive environments hinders their further applications[1–6]. Theoretically NdFeB magnets are composed of three phases: the ferromagnetic matrix phase (Nd$_2$Fe$_{14}$B), which represents about 87% of the magnet volume and the most corrosion sensitive Nd-rich phase and the B-rich intergranular phase[7,8]. This means that NdFeB magnets are prone to galvanic corrosion, in particular, intergranular corrosion attack.

Many investigations have been employed to improve the corrosion resistance of NdFeB magnets, such as the alloy additions and surface coatings. Compared with adding trace elements to improve the corrosion resistance of NdFeB itself[9–11], the surface coatings technology is still the most effective measures[12–16]. However, the electroplating pretreatment is very crucial in the protection process of NdFeB magnets. On the one hand, oils and harmful gases will be adsorbed in the pore on the magnet surface during the machining process, which result in poor adhesion between NdFeB magnets with the coatings. On the other hand, not only the magnetic original size will be seriously changed but the pore and selective corrosion will occur along the grain boundary if the substrate is excessively corroded during the pretreatment process, which will reduce the service life of NdFeB magnets. Therefore, taking reasonable pretreatment process to clean and activate the magnet surface is very necessary.

In this paper, the electroplating pretreatment conditions of NdFeB magnets were simulated and the purpose was to obtain the more suitable electroplating parameter of NdFeB permanent magnets.

1 Experimental

In this study the purity of 99.9% Nd, Fe, B were chosen as raw materials. NdFeB magnets were prepared by conventional powder metallurgy technique including cold isostatic pressing and 1050–1100 ºC sintering using jet milled alloy powder. The magnets used in further measurement were L10 mm×W10 mm×H2 mm, and were removed oil in 2 mol/L NaOH solution.

Pickling process was conducted in the PVC cell which was divided into ten equal spaces with PP board, the samples were fixed between the adjacent plate. The pickling device is shown in Fig. 1((a) Front view; (b) Planform). Pickling solution is prepared with deionized water and analytical nitric acid, and the concentration was 0.5, 1, 2, 4, 5, 6, 8 and 10 mol/L respectively. During the pickling process the temperature inside the cell was about 293 K.
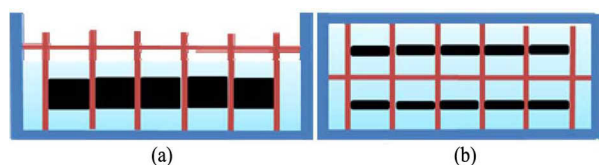
Fig. 1 Pickling device
(a) Front view; (b) Planform

Precoating process was conducted in a conventional three-electrode device at about 293 K. A saturated calomel electrode $Hg/Hg_2SO_4/SO_4^{2-}$ (SCE) and a platinum foil (the purity of 99.99%, the specification is L30 mm×W30 mm×H2 mm) served as reference and counter electrode, respectively. NdFeB magnets were as the precoating cathode. The precoating solution was composited of $NiSO_4$ 280 g/L, $NiCl_2$ 50 g/L, H_3BO_3 50 g/L, SB-1H 0.8 mol/L, D-2 1.2 mol/L, the solution temperature was about 323 K, pH was 4.3 and the precoating time was from 10 to 30 min.

The concentration of each element in the solution was analyzed with inductively coupled plasma-atomic emission spectrometry (ICP-MS) (type Optima2100). The surface hardness was characterized using a micro hardness tester (MHT) (type HV-1000), the morphology of magnets was observed using a field emission scanning electron microscope (SEM), the composition of the precoated was analyzed with an Oxford energy detective spectrometer (EDS) (type S-4800). The electrochemical behavior (electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization) during the precoating process was studied by electrochemical workstation (ECW) (type M273A).

2 Results and discussion

2.1 Pickling technology

2.1.1 Corrosion mechanism

Two kinds of pickling process were performed respectively, one was the ordinary pickling (no ultrasonic) and the other was putting the pickling PVC cell into the ultrasonic generator. Fig. 2 shows the relations among Nd, Fe, B element concentration (*C*) in the solution, the pickling solution concentration (*c*) and the pickling time *(t)*. It can be seen that (Fig. 2(a)) Nd, Fe, B element concentration is respectively less than 5 µg/mL after picking for 120 s as *c* in range of 0.5–4 mol/L. That is to say, under these conditions the magnet corrosion is slow. With *c* increasing from 4 mol/L to 10 mol/L the elements concentration in the solution enhanced significantly. Comparing the content of each element, the relations of *C-c* is $C_{Nd}>C_B\approx C_{Fe}$ as 6 mol/L$\geq c\geq$0.5 mol/L and that $C_{Nd}>C_B>C_{Fe}$ as 10 mol/L>$c\geq$8 mol/L after pickling 300 s. This suggests that Nd-rich phase and B-rich intergranular phase are preferential corrosion in these concentration
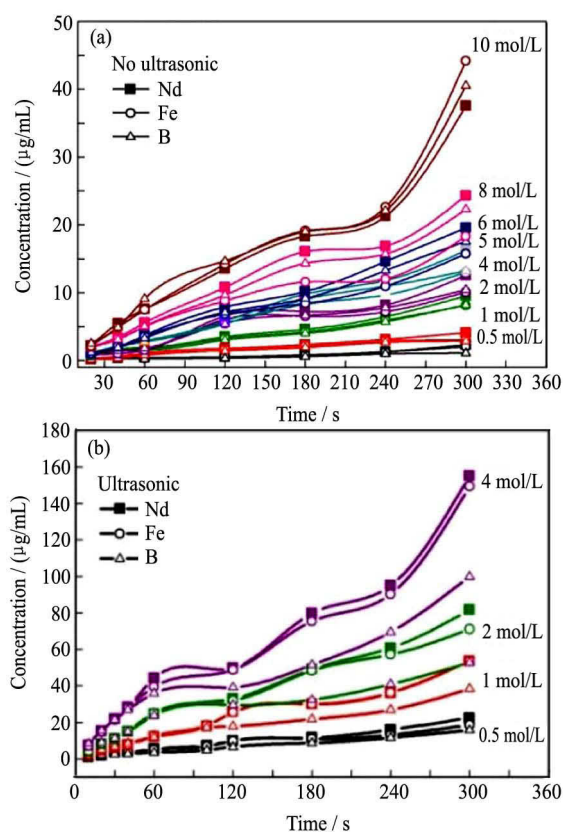

Fig. 2 Relation of element concentration, pickling solution
concentration and pickling time
(a) Ordinary pickling (no ultrasonic); (b) Ultrasonic environment

ranges. In addition when *c*=10 mol/L the elements concentration linearly increase, and the relations is $C_{Fe}>C_B>C_{Nd}$. In other words, under this concentration the matrix phase $Nd_2Fe_{14}B$ begins to corrode.

According to Fig. 2(b) Nd, Fe, B element concentration is higher than 10 µg/mL after picking for 30 s when *c* is in range of 0.5–1 mol/L. Moreover, Nd, Fe, B element concentration approximates to linearly increase after pickling for 120 s as *c*$\geq$2 mol/L, in particular, comparing with the ordinary pickling C_{Nd}, C_{Fe} increase by more than 10 times respectively. These results reveal that NdFeB main phases and the grain boundary are more vulnerable in the ultrasonic environment.

In order to further understand the corrosion mechanism of different pickling systems, the differential transformation is conducted between element concentration (*C*) and the pickling time (*t*) ($v = \dfrac{dC}{dt}$). As seen from Fig. 3 the value $\dfrac{dC}{dt}$ of each element shows a linear increase with increasing of *C*, especially as *C*$\geq$4% mol/L in the ordinary pickling process (Fig. 3(a)). In other words, under this conditions the magnet corrosion quickens. This result can also be confirmed by Fig. 2(a). Therefore, we can use the formula $v = \dfrac{dC}{dt}$ to indirectly estimate the